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The Crystal Structure of NaBa, an Interpenetrating Network of Sodium Tetrahedra and Barium Octahedra

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The crystal structure of NaBa has been determined from single-crystal X-ray diffraction data on X-ray capillary size samples cooled from 200 °C at a rate of 1 °C h^{-1} [cubic, space group $Fd\bar{3}m$, $a = 17.027(3)$ Å, structurally related to $CdNi_{1-x}$ and $NiTi_2$].

Addison[1] has shown that liquid alkali metals due to their low melting points are, in spite of their chemical reactivity, effective in solvating other metals at relatively low temperatures. Barium metal in particular dissolves well in liquid sodium, and this solution absorbs nitrogen[2] readily, eventually precipitating Ba_2N. In this way, the chemistry of barium can be studied using lower temperatures and yielding products of better crystallinity. In our investigations using a liquid sodium–barium alloy, we have produced single crystals of $NaBa_3N$,[3] other sodium–barium nitrides,[4] and BaH_2,[5] suitable for structure determination. For further crystallographic investigations, it became necessary to examine more closely the intermetallic phases formed by the two metals. We have previously reported the structure[6] of Na_2Ba, which is isostructural with Zn_2Mg, one of the well known hexagonal Laves phases. Here we report the structure of NaBa the second of the two known barium–sodium intermetallic compounds.

The existence of NaBa from thermodynamic data has been known for some time. Remy *et al.*[7] reported that NaBa congruently melts at 510 °C. More recently, two independent investigations[8,9] of the Ba–Na phase diagram concluded that NaBa incongruently melts at 197 °C. Stevens and co-workers[9] reported a diffraction pattern, without information about intensities, for NaBa with a tentative orthorhombic cell, and concluded that NaBa has substantial sodium solid solubility up to 79 atom% sodium. The structure of NaBa that we report conforms to 23 of the 25 previously reported diffraction lines, but shows no signs of sodium solid solubility.

The compound NaBa[†,‡] is isostructural with $CdNi_{1-x}$,[11] except that NaBa has no sodium vacancies whereas $CdNi_{1-x}$ requires four vacancies in the 48 Ni positions ($x = 0.083$). The atom positions in NaBa are also the same as those in the more frequently observed $NiTi_2$ structure type;[12] the Ba atoms are on Ti(2) positions and are fourteen-co-ordinate with 6 Na and 8 Ba near neighbours, while the Na atoms are on the Ti(1) and Ni positions, both being twelve-co-ordinate sites with 6 Na and 6 Ba near neighbours. The Ti(2) positions in $NiTi_2$ differ considerably from the Ti(1) positions in terms of their co-ordination spheres. For instance the nearest Ti–Ni distances are 15% longer for Ti(2) than for Ti(1). Barium fits naturally on the Ti(2) sites, giving average Ba–Ba, Ba–Na and Na–Na distances of 4.54, 4.27 and 3.72 Å respectively, which are comparable with those found in Na_2Ba of 4.52, 4.32 and 3.70 Å respectively.[6] These distances are also consistent with the sum of (twelve-co-ordinate[13]) metallic radii 4.49, 4.15 and 3.82 Å respectively which, along with the fact that the molar volume of NaBa is 99.9% that of the metals, $V_{Na} + V_{Ba}$, indicates that there is a slight packing efficiency and only little chemical interaction between the elements as also seen in Na_2Ba.

Fig. 1(*a*) depicts the barium atom sublattice and Fig. 1(*b*) the sodium atom sublattice of NaBa. The barium atoms form a network of empty face-sharing regular and irregular octahedra, where the irregular octahedra are slightly smaller. The smaller barium octahedra share corners and faces with the larger octahedra. The sodium atoms form tetrahedra distributed between the barium octahedra. The tetrahedra of Na(1) atoms are capped on each face by a Na(2) atom, and each Na(2) atom

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[†] Sample preparation. A Pyrex glass tube with joint was narrowed, drawn to *ca.* 0.3 mm outer diameter, and finally sealed at the end in order to make X-ray capillary size samples. Sodium (0.0550 g) and barium metal (0.0806 g) (80.4 mol% Na), were melted together, and drawn into the capillary at 190 °C. After cooling, lengths of capillary were cut, inserted into standard X-ray capillaries of 0.5 mm diameter and sealed under nitrogen. Crystals were then grown by cooling the samples from 200 °C to room temperature at a rate of 1 °C h^{-1}. The same samples used to determine the crystal structure of Na_2Ba were used to determine the structure of NaBa, with the exception that the particular sample in which a suitable NaBa crystal was found was finally sealed under nitrogen instead of argon. Further experimental details are given in ref. 6.

[‡] Crystal data. NaBa, $M = 160.33$, cubic, $a = 17.027(3)$ Å, $U = 4936.4(9)$ Å^3 (by refinement on diffractometer angles for 24 reflections, $\lambda = 0.710\,73$ Å), space group $Fd\bar{3}m$ (no. 227), $Z = 48$, $D_c = 2.59$ g cm^{-3}, $F(000) = 3227$, $\mu = 9.498$ mm^{-1}. A crystal was found at the tip of the sample, but could not be visibly identified. It was clear from the rotation and axial photographs that other crystals and some powder due to the subnitride[4] Na_5Ba_3N were also in the X-ray beam. Therefore, more data were collected than necessary in order to minimise statistically inaccuracies due to stray reflections from other crystals. Data were collected on a CAD4 diffractometer, with Mo-Kα radiation, graphite monochromator, ω scan and $T = 293(2)$ K. 1252 Reflections were measured ($2.0 \leqslant \theta \leqslant 22.9°$, $\pm h, \pm k, \pm l$), 197 being independent [merging $R_{int} = 0.094$ after empirical (ψ scan) absorption correction]. Intensity control: two standard reflections, with no crystal decay.

Structure analysis and refinement. Direct methods, full-matrix least-squares refinement on F^2 (SHELXL-93 for VAX[10]), $w = 1/[\sigma^2(F_o^2) + 139.0128p]$ where $p = \frac{1}{3}[\max.(F_o^2,0) + 2F_c^2]$; $I < 2\sigma(I)$ omitted for refinement (found for three independent reflections); 10 parameters, extinction coefficient = 0.046(3); Ba in 48f, $x = 0.3156(1)$, Na(1) in 32e, $x = 0.2946(3)$, Na(2) in 16d. Final R values: $R1 = 0.044$, $wR2 = 0.061$ [$I > 4\sigma(I)$]; $R1 = 0.066$, $wR2 = 0.075$ (all data). Atomic coordinates and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

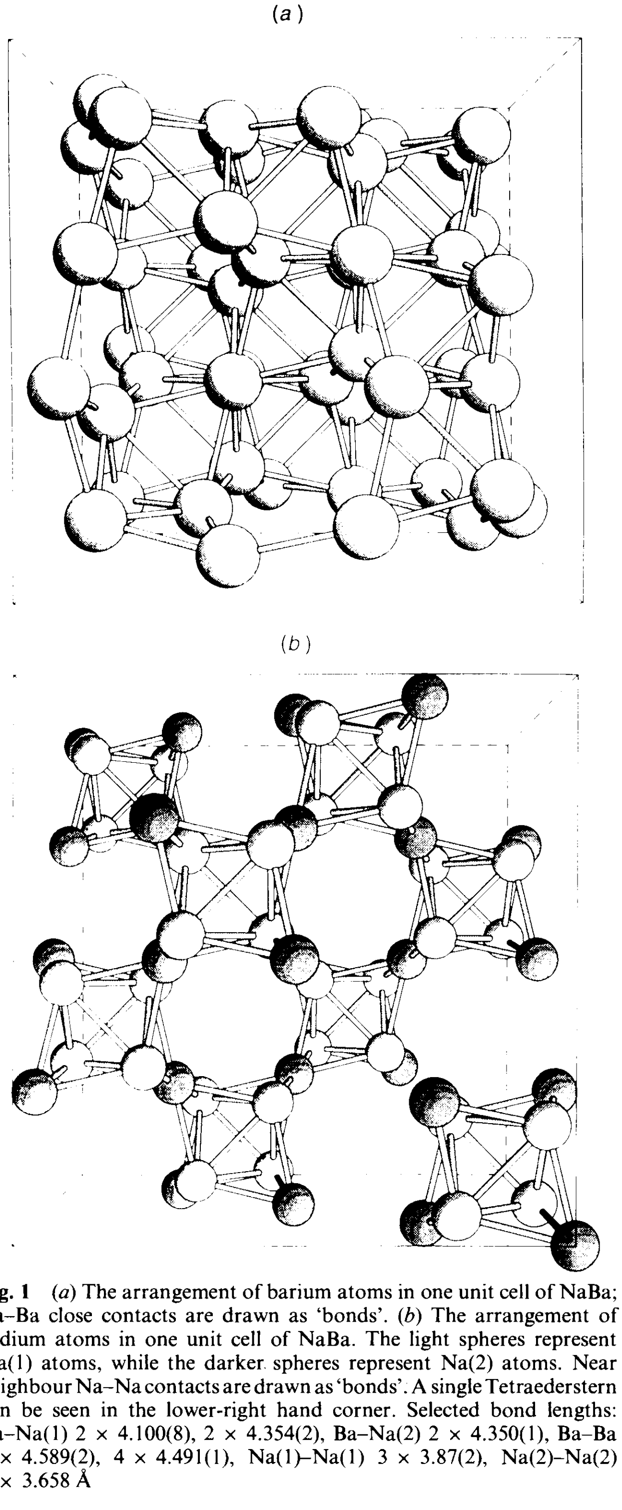

Fig. 1 (*a*) The arrangement of barium atoms in one unit cell of NaBa; Ba–Ba close contacts are drawn as 'bonds'. (*b*) The arrangement of sodium atoms in one unit cell of NaBa. The light spheres represent Na(1) atoms, while the darker spheres represent Na(2) atoms. Near neighbour Na–Na contacts are drawn as 'bonds'. A single Tetraederstern can be seen in the lower-right hand corner. Selected bond lengths: Ba–Na(1) 2 × 4.100(8), 2 × 4.354(2), Ba–Na(2) 2 × 4.350(1), Ba–Ba 4 × 4.589(2), 4 × 4.491(1), Na(1)–Na(1) 3 × 3.87(2), Na(2)–Na(2) 3 × 3.658 Å

caps the faces of two such Na(1) tetrahedra, thus linking the network of sodium atoms.

This eight-atom grouping of sodium atoms found in NaBa, called a Tetraederstern (tetrahedron star) by Schubert,[14] is one that is frequently found in intermetallic compounds. In NaBa these Tetraedersterne of sodium atoms share apices as also found in the tungsten atom framework of, for example, 'β-W' (A15 structure type).

Such empty barium or strontium octahedra are also found in Ba_6Mg_{23}, Sr_6Mg_{23} and $Sr_9Mg_{38}(SrMg_4)$,[15] where the shortest Ba–Ba or Sr–Sr distance is again much like those in the pure metal, *e.g.* 4.40 Å for Ba_6Mg_{23}. If the irregular barium octahedra in NaBa were filled, the Fe_3W_3C structure type would be formed. Many nitrides are also found with this structure type, *e.g.* $Fe_3(Mo,Nb)_3N$ and $Cr_3(Ta,Nb)_3N$, so one might expect nitrogen or some other non-metal impurity to be present in NaBa. We find, however, a residual electron density of less than 0.29 e Å^{-3}, at this position, and only 0.51 e Å^{-3} at the centre of the regular octahedron. Furthermore, one would expect a non-metal atom at this position to cause a contraction of the Ba–Ba distances around it. This is observed for example in BaH_2,[5] and all sodium barium subnitrides such as $NaBa_3N$[3] where the closest Ba–Ba contacts are 4.035 and 3.645 Å respectively. (The longest nearest neighbour Ba–Ba distance in a Ba–Na–N ternary phase is 3.99 Å, found in the isolated Ba_6N octahedra of $Na_{16}Ba_6N$.[16]). Since this is not the case for NaBa, we can at this point omit any impurity atoms at full occupancy. If, however, impurity atom sites were only partially occupied, we would then expect a split position due to a local contraction of the metal-atom co-ordination polyhedron around the impurity atom leading to highly anisotropic displacement parameters. Since the electron distribution of the barium atom is spherical, we conclude that our crystal and the powder of Stevens and co-workers[9] are essentially free of an impurity. The competing Ba–Na–N phases such as Na_5Ba_3N, seen as a powder in X-ray photographs of our sample, must take the nitrogen allowing the binary intermetallic to form.

The refinement of our data shows no indication of either Na vacancies as would be analogous with $CdNi_{1-x}$ of Ba vacancies (or replacement with Na) which would be required for Na solid solubility as suggested by Stevens and co-workers.[9] When allowed to vary (concurrently with the displacement parameters), Na(1), Na(2) and Ba occupancies refine to 1.06(10), 1.11(12) and 1.00(9) respectively, *i.e.* we find full occupancy within standard deviations.

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